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STUDIES ON THE PHOTOCHEMICAL SYNTHESIS OF HYDRAZINE AND OTHER ENDOTHERMIC COMPOUNDS

Status Report

for the period 15 April to 15 June 1954

by

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with

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A. THE PHOTOCHEMICAL SYNTHESIS OF HYDRAZINE FROM AMMONIA

The results of our investigations of the photolysis of ammonia at 1849 Å under both static and dynamic conditions were submitted to the Journal of Chemical Physics some time ago. The paper appeared in the May 1954 issue of the journal.

A manuscript covering the salient features of our studies of the mechanism of hydrazine formation in the reaction of ammonia with Hg $6(^3P_1)$ atoms has been prepared. It will be submitted shortly to the Journal of Chemical Physics.

B. THE MERCURY-$6(^3P_1)$-PHOTOSENSITIZED DECOMPOSITION OF ETHYLENEIMINE

This reaction has been studied at 25°C under circulating conditions. The principal products of the reaction have been shown to be ethylene, nitrogen and hydrogen. Small amounts of butanes, methane and a polymeric material have also been isolated. The analyses were largely carried out on the mass spectrometer. The rates of formation, and the quantum yields for the principal products of the reaction have been determined as functions of both substrate pressure and duration of exposure. At the present time, the date are in process of evaluation toward the development of a mechanism for the reaction. As soon as a reasonable mechanism can be formulated, the results of the study will be submitted to ONR as a technical report.

C. THE PHOTOOXIDATION OF CHLORATE TO PERCHLORATE

A number of experiments have been performed on the irradiation of suspensions of zinc oxide in dilute potassium chlorate solutions in the

presence of oxygen. The reactions were carried out in Pyrex vessels perfused with the radiation from a quartz mercury arc. Since the Pyrex absorbs all wavelengths shorter than 3200 Å, and the zinc oxide does not absorb above 4000 Å, the actinic energy can be considered as essentially arising from the strong 3660 Å group from the arc. A major problem encountered early in the investigation was the analysis for perchlorate in the presence of chlorate. At the present time, our efforts are being devoted exclusively to the analytical aspects of the problem. It is expected that the technique used will shortly be refined sufficiently to enable quantitative determination of the small amounts of perchlorate ion present after irradiation. Thereafter the kinetic studies will be resumed.

D. THE PHOTODECOMPOSITION OF TITANIUM TETRACHLORIDE

A flexible high-vacuum reaction assembly has now been constructed for the study of the photodecomposition of titanium tetrachloride, in the gas phase, under flow conditions. Mercury vapor will be used as a getter for chlorine atoms in the reaction. Analytical methods for quantitative determination of the lower halides of titanium are also being explored.

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